

Property Retention Studies of Tough Hybrid Urethane Resin Systems

by

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Abstract

This paper describes the development of a high strength urethane hybrid resin system designed to obtain high reactivity and chemical resistance. A study was initiated to investigate the inherent advantages of a new development on urethane acrylate hybrid resin systems and their properties compared to unsaturated polyester and vinyl ester resins systems. The resin presented in this paper is a one component hybrid urethane resin system which provides a simple system adaptable to use with common formulations that process with fast reaction times and high filler loadings when required. Comparative mechanical properties of composite substrates based on the hybrid urethane were investigated. Mechanical property retention of the urethane hybrid system after exposure to various corrosive environments was studied for up to 60 weeks.

Introduction

Unsaturated polyesters are the type of thermosetting resin systems that can be easily used in the preparation of composite materials. The simplicity of modifying viscosities and curing times on this line of resins make them more practical to use in a large variety of applications. However, the mechanical properties of unsaturated polyesters can not reach the performance levels necessary to meet some of today's crucial application demands. The mechanical properties of unsaturated polyesters are greatly improved by introducing polyurethanes into the thermosetting networks. One problem associated with the preparation of polyester-polyurethane hybrids, is commonly known as "gassing". The gassing, or generation of small bubbles in the composite materials, is associated with trace amounts of water or residual acid content in the unsaturated polyester. The approach presented in this paper addresses the preparation of a thermosetting polyurethane resin system that eliminates problems during the curing process such as gassings or short pot life.

Discussion

To improve the properties of unsaturated polyesters, approaches have included the addition of high performance polymers that can enhance the strength and toughness of the system. For more stringent mechanical strength requirements, switching to vinyl ester or polyurethane resin systems may be necessary. Polyurethane resins provide the best mechanical properties of this group, but certain aspects must be considered before selection. Standard polyurethane resins are two part systems consisting of a polyol and polyisocyanate. Once mixed, their effective working time is extremely limited (minutes) which makes its use virtually impossible in open type baths. In-die resin injection is the only viable means of processing. The high sensitivity of isocyanates to moisture can ultimately impact its performance and influence final properties. In general, isocyanates and polyols readily react at ambient temperature making a one pack system unfeasible. The two components must be kept separate prior to mixing. Once mixed, the resulting blend becomes unstable yielding a very short pot-life. This is a result of viscosity build from the fast reaction between the polyol and the polyisocyanate that ultimately creates a high molecular weight polymer.

The effects of residual water, acid groups from the polyester resin, and a variety of additives from promoters to catalysts and release agents must also be taken into account. In most cases, the effect of additives is adverse to stability, i.e., it speeds up the process of molecular weight built up and thus decreases pot-life. Carroll¹ et al, for example, reported the drastic effect that mold release alone plays on the stability of the polyurethane system.

Several approaches have been investigated to provide a one component urethane resin system in which the reacting materials are combined prior to use and then reacted. For example, a prepolymer from an isocyanate can be converted to intermediates that regenerate the isocyanate upon heating. Other approaches include the addition of acid chlorides² to increase the stability of the mixtures to up to 11 hours. Combinations of amines or organic acids and organo tin compounds have been claimed to stabilize urethanes for up to one hour³ before the mixture cures. Block isocyanates⁴ have also been used as an attempt to increase the pot stability of urethanes before they gel and harden. However, these systems do not eliminate the problem of moisture sensitivity.

As an alternative to the open bath used in pultrusion, an interesting approach was reported in a European patent application⁵ that allows the isocyanate intermediates to be isolated in a close container. The fibers are pulled through the container allowing them to impregnate, the excess of resin is removed outside the container and return to the container. In addition, a catalyst is added onto the surface of the impregnated fibers to

accelerate the curing and formation of urethanes and/or isocyanurate linkages. This approach may expose fibers entering the impregnation chamber and the forming die to moisture.

The approach reported in this paper is aimed at combining the high reactivity and processing characteristics of traditional polyester and vinyl ester resin systems with the toughness of polyurethanes. In addition, this system eliminates the draw back of the isocyanate reaction with moisture, thereby permitting its use in the open bath process and not limiting its use to close systems only. These resins are designed to combine properties inherent of polyurethanes with the reactivity of vinyl esters and unsaturated polyesters. The system studied is provided as one component and does not need to add isocyanates to the resin to form urethanes.

The chemistry used in the preparation of the one component hybrid urethane resin system allows positioning the appropriate amount of reactive groups that are able to crosslink with the styrene monomer. The amount of reactive groups that crosslink with the styrene monomer can be varied to allow the appropriate crosslinking of the system. Toughness and heat distortion temperature may be modified according to the reactive group concentration. Urethane linkages are formed during the preparation of the resin eliminating additional steps of adding isocyanates to form urethanes as it does in typical polyurethane processes. This resin eliminates the risk of foaming due to the reaction of isocyanates with moisture since the isocyanates that form the urethane are already pre-reacted.

Conventional urethane forming reactions are sensitive to moisture and lead to undesirable side reactions with water leading to the formation of carbon dioxide gas within the polyurethane during its production. The gas bubbles give rise to increased porosity in the composite products. Pre-reacting the isocyanate within the polymer to form the present system eliminates the problems associated with the handling of a two component system. Therefore, no special equipment is necessary to handle the resin mixtures.

The single component urethane system is cured with a variety of conventional peroxides and the mixtures have excellent catalyzed stability at ambient temperature. The stability associated with this resin is of particular importance for open or close mold applications that require traditional processing techniques such as open bath and perform injection. Conventional polyurethane systems cannot be processed using these techniques.

The reactive hybrid urethane resin system is dissolved in styrene. This hybrid urethane and styrene solution allows easy handling and provides excellent wet-out of glass fiber and fillers when added. The interaction of the resin with the fiber and fillers provides substantial improvement in the physical properties. In addition, the urethane functionality contained within the polymer and

the designed unsaturation, combine to deliver improved overall composite part performance. Impact performance is enhanced over conventional polyester and vinyl ester resins minimizing crack resistance of finished parts. The resin is formulated to provide finished products with smooth low-profile like surface characteristics which exhibit unique fiber hiding capability.

The reactive hybrid urethane resin can be tailored to bring attributes of high strength to weight and stiffness to weight ratios. The appropriate amounts of reactive groups on the polymer crosslink with the styrene monomer to generate a network with improve chemical resistance to selected chemical environments. Studies on the chemically exposed composites prepared from these crosslinked materials were undertaken to understand their property degradation and damage development.

Experimental

The profile selected for testing consisted of a traditional flat panel .250-inch thick by 8-inches wide and was produced via the pultrusion process. This configuration permitted both longitudinal (lengthwise) and transverse (crosswise) property testing.

The composition of the test panels consisted of the urethane hybrid base resin discussed previously. Curing was accomplished using a combination of low, medium and high 10-hour ½-life peroxide initiators. Other additives included pigment, an internal mold release, UV stabilizer and inorganic filler. In addition to the formulated resin system, the remaining fibrous portion consisted of a synthetic surfacing veil and a combination of continuous strand mat, bi-directional fabric and unidirectional fiberglass roving. The combined fiberglass reinforcement resulted in an approximate 65% weight fraction.

The resulting panels were cut into 12" sections. All cut edges were edge coated using a modified bisphenol "A" corrosion resistant unsaturated polyester resin containing paraffin in accordance with ASTM C-581, Section 6.5.3.

Exposure Conditions

The following testing parameters were chosen for these preliminary studies to determine the chemical resistance and durability of the single component hybrid urethane resin system discussed herein..

- Alkali Resistance
- Water Resistance
- Salt Water Resistance

Alkali Resistance - The pH 12.4 alkaline solution was prepared with Calcium Hydroxide using a Mettler DL25 Autotitrator instrument calibrated with certified pH buffer solutions. The solution was tested weekly and adjusted as necessary to maintain the appropriate pH level.

Test panels were totally immersed in the saturated solution at 24° C (75° F) for the designated intervals discussed later.

Water Resistance - A water bath was prepared in accordance with ASTM D-2247. Test panels were exposed to an environment maintained at 100% relative humidity and 38° C (100° F). Relative Humidity was measured using a VWR Digital Hygrometer/Thermometer. Additional water was added as necessary to maintain the consistency of the bath. Test coupons were suspended above the liquid portion permitting an even atmosphere around each coupon.

Salt Water Resistance - The salt water solution was prepared in accordance with ASTM D-1141. The salinity was adjusted to the prescribed a specific gravity range of 1.020 – 1.023 using a hydrometer. The solution was tested weekly and refreshed as necessary. Panels were totally immersed at 24° C (75° F).

Physical Testing Procedure

The following test methods were used to determine the selected mechanical properties of the laminates studied.

- **ASTM D-638** Standard Test Method for Tensile Properties of Plastics
- **ASTM D-790** Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials
- **ASTM D-2344/D-2344M** – Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates

Tensile strength, modulus and % elongation were determined in both the longitudinal (lengthwise) and transverse (crosswise) directions. Flexural strength and modulus were determined in both the longitudinal and transverse directions. Shear strength and modulus were determined in the primary fiber direction only.

Baseline or reference mechanical properties were determined from panels produced for this evaluation. A minimum of twenty samples were tested in order to establish the baseline statistical information. Panels exposed to the conditions described within were extracted from conditioning tanks after six, eighteen and sixty weeks. Each panel was cleaned and examined in accordance with ASTM C-581. The panels were then cut and tested per the procedures discussed above.

Results and Discussion

This evaluation was initiated to determine if hybrid urethane resin systems, although mechanically

stronger than traditional polyester and vinyl ester resin systems, could withstand some of the more stringent environments they may encounter for today's new applications. These tests were not performed to compare the hybrid urethane resin system to other resin types for corrosion resistance in this evaluation, but to merely determine if their use would be feasible for these new applications.

Figure 1 and 2 shows the results of the preliminary comparative screening. Laminar shear strength and shear modulus were determined on laminates produced via the pultrusion process. The results show a substantial improvement in properties on both single and two component urethane systems over conventional resins such as isophthalic polyester and the vinyl ester. The highest properties were obtained with the two part urethane system. However, the one component urethane system does not require the considerable investment in metering equipment and injection dies necessary to process the two component urethane. In addition, the problem of controlling the moisture content in the polyol portion of the two component system is eliminated by the processing characteristics of the one component hybrid resin. From these assessments, the first phase of this property retention study was focused on the single component urethane hybrid resin system only.

The following figures compare baseline mechanical properties to the properties determined after exposure to the various environments discussed. Each graph shows retention of these properties after six, eighteen and sixty week's exposure.

Figure 3 shows the % Property Retention for Tensile Strength in the longitudinal direction. In this Figure the least effect on the composite sample containing the hybrid resin was with the salt solution. The % retention of the salt solution after 60 weeks was 93%. Humidity on the other hand, had the most effect with a % retention of about 83 after 60 weeks. The alkali solution had about 88 % retention after 60 weeks. All values were above the well accepted values by Industry of 50% retention after 52 weeks.

Figure 4 shows the % Property Retention for Tensile Strength in the traverse direction. In this Figure the salt solution and the alkali solution show very close retention performance with a % retention higher of 95 after 60 weeks. The results for the humidity values showed a 90 % retention after 60 weeks.

Figure 5 shows the % property retention for Flexural Strength in the longitudinal direction. Salt solution showed a nearly 100 % retention after 60 weeks. A somewhat reversed behavior was observed in property retention for humidity and alkali as compared to tensile strength evaluations. In this case humidity had better property retention than alkali. For all samples tested in salt, alkali and humidity solutions, the % property retention exceeded 85 % after 60 weeks.

Figure 6 shows the % Property Retention for Flexural Strength in the traverse direction. The salt solu-

tion, the alkali solution and humidity showed very close results in the % property retention. All values were in the range of 82 to 87 % retention.

Figure 7 shows results for the % Property Retention for the Shear Strength. All samples testes in salt, alkali and humidity showed an excellent % retention of about 95%.

Conclusions

Mechanical strength evaluations on laminates prepared with urethane based resins showed substantial improvement over tradition polyester and vinyl ester systems. The urethane hybrid system evaluated, provided excellent property retention after long term exposure to various harsh environments. The merits gleaned from these few elementary evaluations will provide fodder for more extensive research studies.

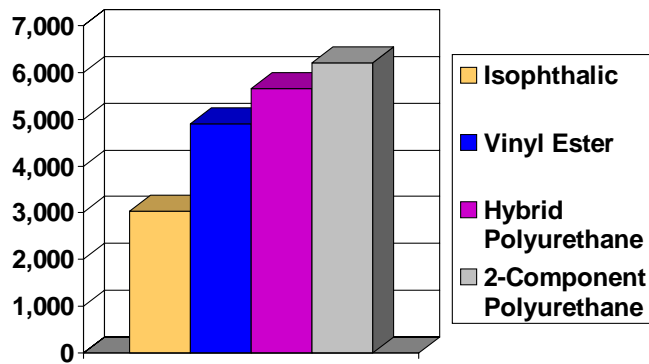


Figure 1 – Laminar Shear Strength comparison of pultruded laminates formulated with the various resins indicated as per ASTM 2344-84

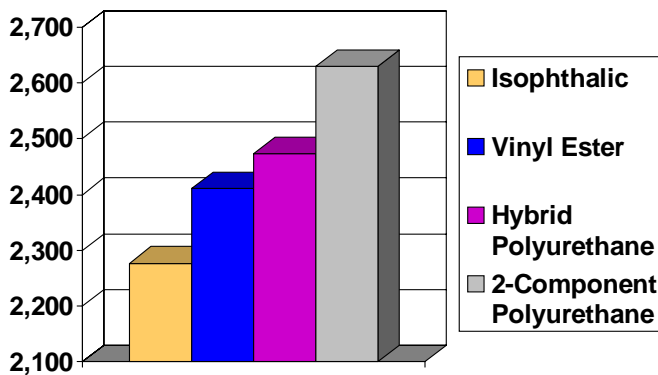


Figure 2 – Laminar Shear Moduli Lengthwise comparison of pultruded laminates formulated with the various resins indicated as per ASTM 2344-8.

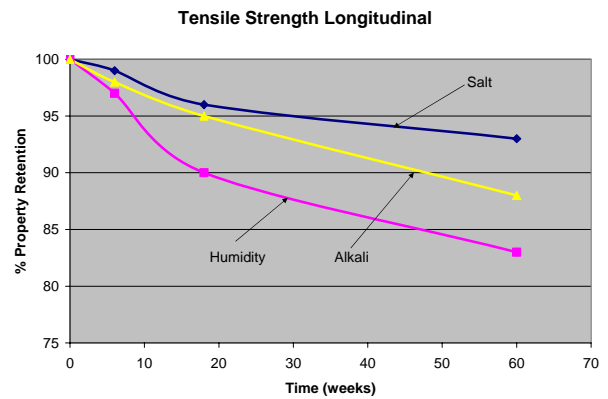


Figure 3 - Tensile Strength longitudinal - % Property Retention.

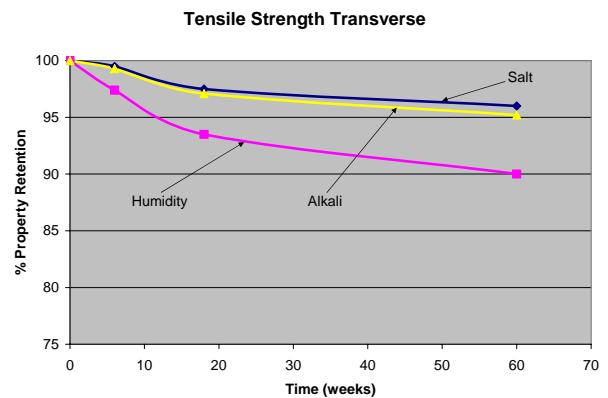


Figure 4 - Tensile Strength Transverse - % Property Retention.

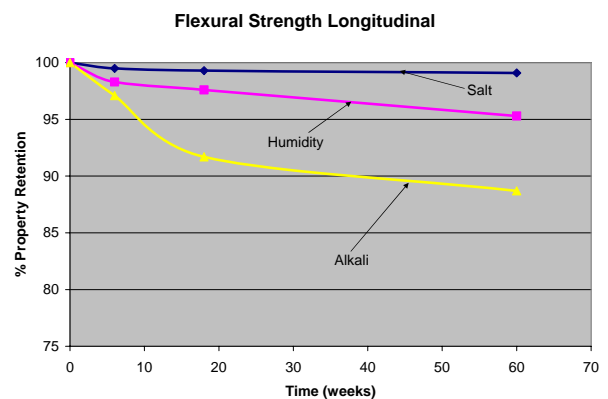


Figure 5 - Flexural Strength Longitudinal - % Property Retention.

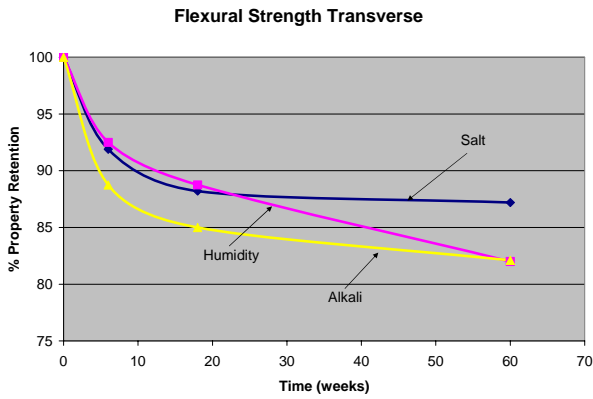


Figure 6 - Flexural Strength Transverse - % Property Retention.

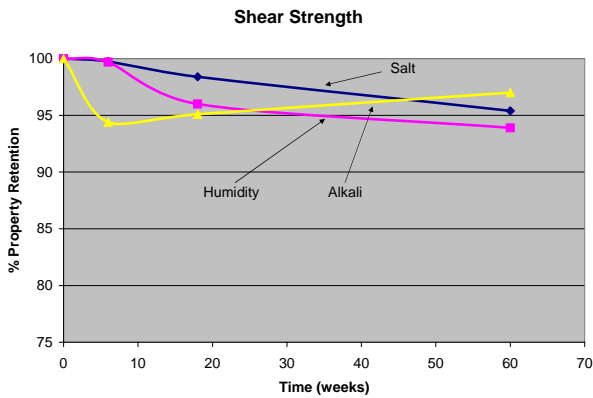


Figure 7 - Shear Strength.

References:

1. Hybrid Polymer networks Based on Unsaturated Polyester Urethane, B. Carroll, S. Walsh and H. Nava, CFA, Composites 2001.
2. US Patent 4,738,991
3. EP Patent 1,048,440
4. C. Chen and C. M. Ma, Composites Science and Technology 52, 427 (1994).
5. WO 02/16482

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